International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C08F 14/18, 20/22, 2/06

A1

(11) International Publication Number: WO 93/20116

(43) International Publication Date: 14 October 1993 (14.10.93)

(21) International Application Number: PCT/US93/01626

(22) International Filing Date: 26 February 1993 (26.02.93)

(30) Priority data:
858,150 27 March 1992 (27.03.92) US

(60) Parent Application or Grant
(63) Related by Continuation
US 858,150 (CIP)
Filed on 27 March 1992 (27.03.92)

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(81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).

Published
With international search report.
With amended claims.

(54) Title: METHOD OF MAKING FLUOROPOLYMERS

(57) Abstract

A process for making a fluoropolymer is disclosed. The process comprises solubilizing a fluoromonomer in solvent comprising a carbon dioxide fluid, and then polymerizing the fluoromonomer to produce the fluoropolymer. A preferred solvent for carrying out the process is supercritical carbon dioxide; preferred fluoromonomers for carrying out the process are fluoroacrylate monomers such as 1,1-dihydroperfluorooctyl acrylate. The polymerization step is preferably carried out in the presence of an initiator such as azobisisobutyronitrile.

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METHOD OF MAKING FLUOROPOLYMERS

Cross Reference to Related Applications

This application is a continuation-in-part of copending U.S. Patent Application Serial No. 07/858,150, filed March 27, 1992.

Field of the Invention

The present invention relates to a method of making fluoropolymers, including copolymers thereof, in a solvent comprising a carbon dioxide fluid such as supercritical carbon dioxide.

Background of the Invention

Chlorofluorocarbons (CFCs) have been identified as one of the main causes of the depletion of atmospheric ozone. As a result, extensive effort has been directed towards discovering alternatives to CFCs in a variety of applications. In addition to the utilization of CFCs as refrigerants and aerosols, CFCs are commonly used as solvents for the manufacture of fluoropolymers, which are generally insoluble in traditional organic s lvents but can often b solubiliz d in CFCs. H nce, there is a need for alternative methods of manufacturing flu ropolymers.

A supercritical fluid (SCF) is a substance above its critical temperature and critical pressure (r "critical point"). Compressing a gas n rmally causes a phase separati n and th appearance of a separate liquid phase. However, if the fluid is in a supercritical state, compression will only result in density increases: no liquid phase will be formed. The physical properties of supercritical fluids are highly unpredictable, and the use of supercritical fluids for carrying out polymerization processes has received relatively little attention.

S. Kumar et al., *Polym. Prep.* 27, 224 (1986), describe the free radical precipitation polymerization of polystyrene chains in supercritical ethane. The styrene monomers were dissolved in ethane and polymerized with azobisisobutyronitrile ("AIBN") as an initiator using an apparatus having a high-pressure optical cell.

V. Sarai and E. Kiran, *Polym. Prep.* 31, 687 (1990), describe the free radical polymerization of styrene in supercritical ethane, propane, and butane, using AIBN, t-butyl peroxide and t-butyl peroxybenzoate as initiators.

K. Scholsky, *Polym. Prep.* 31, 685 (1990), describe a variety of polymerization reactions using supercritical fluids. The article summarizes publications on the polymerization of fluorinated olefins, such as vinyl fluoride, tetrafluoroethylene, the copolymerization of tetrafluoroethylene and sulfur dioxide, and polyperfluoropropylene. Other fluorinated olefins mentioned include n-tetradecafluoroheptene-1, n-perfluoropentadiene-1,4, vinylidene chlorofluoride, and a variety of vinylic monomers. The polymerization of fluoropolymers in carbon dioxide is not suggested.

E. Beckman and R. Smith, *J. Phys. Chem.* 94, 345 (1990) describe th micr emulsi n polymerization of acrylamide ($CH_2CHCONH_2$) in supercritical fluids, and

particularly the inverse microemulsion p lymerization of water-soluble acrylamid monomers within near-critical and sup rcritical alkane continuous phases.

G.S. Varadarajan, *Fre Radical Polymerization in Supercritical Fluid Solvents* (November 29, 1990) (MIT Doctoral Thesis) describes the free radical polymerization of polymethylmethacrylate (MMA)(CH_2=C(CH_3)$COOCH_3$) in supercritical carbon dioxide using AIBN as an initiator. The polymerization of fluoromethacrylates in supercritical carbon dioxide is not suggested.

Canadian Patent No. 1,274,942 is directed to acrylic acid polymerization by homopolymerizing carboxylic acids such as acrylic acid and methacrylic in supercritical carbon dioxide. The polymerization of fluoroacrylate or fluoromethacrylate monomers in supercritical carbon dioxide is not suggested.

V. Krukonis and M. McHugh, *Supercritical Fluid Extraction*, 156-158, describes the fractionation of a perfluoroalkylpolyether oil and a chlorotrifluoroethylene oligomer in supercritical carbon dioxide, but does not suggest the polymerization of fluoromonomers in supercritical carbon dioxide.

Summary of the Invention

A process for making a fluoropolymer is disclosed. The process comprises solubilizing a fluoromonomer in a solvent, the solvent comprising carbon dioxide fluid; and then polymerizing the fluoromonomer in said solvent to produce said fluoropolymer. The fluoromonomer may be a fluoroacrylate monomer, a fluorostyrene monomer, a fluorinated vinyl ether monomer, or a fluoroalkylene oxid oligomer. Fluoromonomers of the type which und rgo free radical polymerizati n ar preferred. Th polymerization reaction is, in general, carried out in the pr sence of an initiator. Th carbon dioxide

fluid may b liquid carbon dioxide or supercritical carbon dioxide.

In one embodiment f th foregoing, the process may further comprise solubilizing a comonomer in the carbon dioxide fluid, with th polymerizing step comprises copolymerizing the fluoromonomer with the comonomer.

The fluoropolymers can be used as a composition for altering surface tension properties, e.g., to create low energy surfaces such as for stain resistance properties.

Brief Description of the Drawings

In the drawings which form a part of the disclosure of the invention:

Figure 1 is a phase equilibria diagram of poly(chlorotrifluoroethylene) in carbon dioxide at 40°C, wherein the x axis of the diagram represents the weight fraction of the sample, and the y axis represents pressure in bars; and

Figure 2 is a phase equilibria diagram of poly(1,1-dihydroperfluorooctyl acrylate) in carbon dioxide at 60°C, wherein the x axis of the diagram represents the weight fraction of the sample, and the y axis represents pressure in bars.

Detailed Description of the Invention

The term "fluoropolymer," as used herein, has its conventional meaning in the art. *See generally Fluoropolymers* (L. Wall, Ed. 1972)(Wiley-Interscience Division of John Wiley & Sons); *see also Fluorine-Containing Polymers*, 7 Encyclopedia of Polymer Science and Engineering 256 (H. Mark et al. Eds., 2d Ed. 1985). Likewise, the term "fluoromonomer" refers to fluorinated precursor monomers employed in th synthesis of flu ropolymers. The term "s lubilizing," as us d herein, is used to indicate that the

fluorom nomers ar in the same phas as the carbon di xid fluid in the pr cess of th present inventi n; hence the polym rization r actions of th present invention are s lution polymerizations, as opposed to heterogeneous polym rizations or bulk polym rizations, with these terms having their ordinary meaning in the industry. *See, e.g.*, G. Odian, *Principles of Polymerization*, 301-334 (3d Ed. 1991)(Wiley Interscience).

Any suitable fluoromonomer may be used, including, but not limited to, fluoroacrylate monomers, fluoroolefin monomers, fluorostyrene monomers, fluoroalkylene oxide monomers (e.g., perfluoropropylene oxide, perfluorocyclohexene oxide), fluorinated vinyl alkyl ether monomers, and the copolymers thereof with suitable comonomers, wherein the comonomers are fluorinated or unfluorinated. Fluoromonomers which are polymerized by a free radical polymerization process are preferred.

Fluorostyrenes and fluorinated vinyl alkyl ether monomers which may be polymerized by the method of the present invention include, but are not limited to, α-fluorostyrene; β-fluorostyrene; α,β-difluorostyrene; β,β-difluorostyrene; α,β,β-trifluorostyrene; α-trifluoromethylstyrene; 2,4,6-Tris(trifluoromethyl)styrene; 2,3,4,5,6-pentafluorostyrene; 2,3,4,5,6-pentafluoro-α-methylstyrene; and 2,3,4,5,6-pentafluoro-β-methylstyrene. These monomers are particularly useful as comonomers in the method of the present invention.

Tetrafluoroethylene copolymers which are amorphous or have low melting points can be prepared by the method of the present invention and include, but are not limited to, tetrafluoroethylene-hexafluoropropylen copolymers, tetrafluoro thylene-perfluorovinyl ther cop lymers (e.g., cop lym rs of tetrafluoroethylen with perfluoropropyl vinyl ether),

tetrafluoroethylene-ethylene c p lymers, and perfluorinated ionomers (e.g., perfluorosulfonate ionomers; perfluorocarboxylate ionomers).

Fluorocarbon elastomers (*see, e.g.*, 7 Encyclopedia of Polymer Science & Engineering 257) are a group of amorphous fluoroolefin polymers which can be produced by the process of the present invention and include, but are not limited to, poly(vinylidene fluoride-*co*-hexafluoropropylene); poly(vinylidene fluoride-*co*-hexafluoropropylene-*co*-tetrafluoroethylene); poly[vinylidene fluoride-*co*-tetrafluoroethylene-*co*-perfluoro(methyl vinyl ether)]; poly[tetrafluoroethylene-*co*-perfluoro(methyl vinyl ether)]; poly(tetrafluoroethylene-*co*-propylene; and poly(vinylidene fluoride-*co*-chlorotrifluoroethylene).

The term "fluoroacrylate monomer," as used herein, refers to esters of acrylic acid ($H_2C{=}CHCOOH$) or methacrylic acid ($H_2C{=}CCH_3COOH$), where the esterifying group is a fluorinated group such as perfluoroalkyl. A specific group of fluoroacrylate monomers useful in the method of the invention are compounds represented by formula (I):

$$H_2C{=}CR^1COO(CH_2)_nR^2 \qquad \text{(I)}$$

wherein:

n is 1 or 2;

R^1 is hydrogen or methyl; and

R^2 is a perfluorinated aliphatic or perfluorinated aromatic group, such as a perfluorinated linear or branched, saturated or unsaturated C1 to C10 alkyl, phenyl, or naphthyl.

In a particular embodiment of the invention, R^2 is a C1 to C8 perfluoroalkyl or $-CH_2NR^3SO_2R^4$, wherein R^3 is C1-C2 alkyl and R^4 is C1 to C8 perflu roalkyl.

The term "perfluorinated," as used herein, means that all or essentially all hydrog n atoms on an organic group are replac d with fluorin .

M nom rs illustrative of F rmula (I) above, and their abbreviations as used herein, include the following:

2-(N-ethylperfluorooctanesulfonamido) ethyl acrylate ("EtFOSEA");

2-(N-ethylperflooctanesulfonamido) ethyl methacrylate ("EtFOSEMA");

2-(N-methylperfluorooctanesulfonamido) ethyl acrylate ("MeFOSEA");

2-(N-methylperflooctanesulfonamido) ethyl methacrylate ("MeFOSEMA");

1,1-Dihydroperfluorooctyl acrylate ("FOA"); and

1,1-Dihydroperfluorooctyl methacrylate ("FOMA").

In the process of the invention, the fluoroacrylate monomers may be polymerized in the presence of a free radical polymerization initiator. Any of the various organic and inorganic initiators which are known for the polymerization of monomers can be used, so long as it is compatible with carbon dioxide. The polymerization is carried out at two different temperatures by first subjecting the monomers to initial polymerization at a lower temperature, and then completing the polymerization at a substantially higher temperature.

Organic free radical initiators are preferred and include, but are not limited to, the following: acetylcyclohexanesulfonyl peroxide; diacetyl peroxydicarbonate; dicyclohexyl peroxydicarbonate; di-2-ethylhexyl peroxydicarbonate; tert-butyl pern od canoate; 2,2'-azobis (meth xy-2,4-dimethylvaleronitrile; tert-butyl perpivalate; dioctanoyl p r xide; dilauroyl per xid ; 2,2'-

azobis(2,4-dimethylvaler nitrile); tert-butylaz -2-cyan butane; dibenzoyl peroxide; tert-butyl per-2-ethylhexanoate; tert-butyl permaleate; 2,2-azobis(isobutyronitrile); bis(tert-butylperoxy)cyclohexane; tert-butyl peroxyisopropylcarbonate; tert-butyl peraceatate; 2,2-bis(tert-butylperoxy)butane; dicumyl peroxide; ditert-amyl peroxide; di-tert-butyl peroxide; p-menthane hydroperoxide; pinane hydroperoxide; cumene hydroperoxide; and tert-butyl hydroperoxide. Preferably, the initiator is azobisisobutyronitrile ("AIBN").

The process of the invention is carried out in a carbon dioxide fluid, e.g., carbon dioxide in a liquid or supercritical state. As will be appreciated by those skilled in the art, all gases have a critical temperature above which the gas cannot be liquified by increasing pressure, and a critical pressure or pressure which is necessary to liquify the gas at the critical temperature. For example, carbon dioxide in its supercritical state exists as a form of matter in which its liquid and gaseous states are indistinguishable from one another. For carbon dioxide, the critical temperature is about 31°C (88°F) and the critical pressure is about 73 atmospheres or about 1070 psi. The term "supercritical carbon dioxide" as used herein refers to carbon dioxide at a temperature greater than about 31°C and a pressure of greater than about 1070 psi.

Liquid carbon dioxide may be obtained at temperatures of from about -15°C to about -55°C and pressures of from about 77 psi to about 335 psi.

One or more solvents and blends thereof may opti nally be included in the carbon dioxide. Illustrative s lvents include, but are n t limited to, tetrahydrofuran, cyclohexan , and methanol. Such

solvents are typically included in an amount, by w ight, of up to about 20%.

Th polymerizati n initiat rs are used in the amounts conventionally employed for polymerizati n. For example, the initiator may be used in an amount of about 0.01 to 10, preferably about 0.01 to 5, parts by weight per 100 parts by weight monomer.

The polymerization reaction may be carried out at a temperature of about -55°C to about 300°C, and is typically carried out at a temperature of about -30 to 100°C. The reaction may be carried out at a pressure ranging from about 15 psi to about 45000 psi, and is typically at a pressure of from about 500 psi to about 10000 psi.

In alternative embodiments of the present invention, at least one monomer or comonomer is solubilized in carbon dioxide and copolymerized with the fluoromonomer. Any suitable monomers or comonomers can be employed, including, but not limited to, acrylate, methacrylate, acrylamide, methacrylamide, styrenics, ethylene, and vinyl ether monomers. The copolymerizations of the present invention may be carried out under temperature and pressure conditions similar to those given above.

The polymerization can be carried out batchwise or continuously with thorough mixing of the reactants in any appropriately designed high pressure reaction vessel (i.e., capable of withstanding pressures up to 45000 psi). To remove the heat evolved during the polymerization, advantageously the pressure apparatus includes a cooling system. Additional features of the pressure apparatus used in accordance with the invention include heating means such as an electric heating furnace to heat the reaction mixture to th desired temperatur and mixing means, i.e., stirrers such as paddle stirrers, impeller stirrers, or

multistage impulse countercurrent agitators, blades, and the like.

The p lymerizati n can be carried out, for example, by placing the monomer and initiator in the pressure apparatus and introducing carbon dioxide in liquid form. The reaction vessel is closed and the reaction mixture brought to the polymerization temperature and pressure. Alternatively, only a part of the reaction mixture may be introduced into an autoclave and heated to the polymerization temperature and pressure, with additional reaction mixture being pumped in at a rate corresponding to the rate of polymerization. In another possible procedure, some of the monomers are initially taken into the autoclave in the total amount of carbon dioxide and the monomers or comonomers are pumped into the autoclave together with the initiator at the rate at which the polymerization proceeds.

When the polymerization is complete the reaction mixture is cooled (if necessary), the carbon dioxide separated off (e.g., by simply venting to the atmosphere), and the polymer collected. After separation of the carbon dioxide, the polymer can be collected simply by physical isolation, or by dissolution and precipitation, for example, by adding Freon-113™ or α,α,α-trifluorotoluene to the polymer to dissolve the polymer and recover it from the reaction vessel and then precipitating the same with methanol.

The following Examples are provided to further illustrate the present invention. In the Examples, SCF means supercritical fluid; AIBN means azobisisobutyronitrile; MMA means polymethylmethacrylate; psi means pounds per square inch; g means grams; mg means milligrams; mL means milliliters; min means minutes; Mw means weight average molecular weight; Mn means number averag mol cular weight; MWD means molecular weight distribution (Mw/Mn); mmol means

millimoles; dL/g means d ciliters per gram; cm means centimeters; THF means tetrahydr furan; DMF means N,N-dim thylf rmamide; DMAc means N,N-dimethylac tamid ; [n] m ans intrinsic viscosity; NMR means nuclear magnetic resonance; GPC means gel permeation chromatography; FTIR means fourier transform infrared; IR means infrared; and temperatures are given in degrees celsius. These examples are illustrative of the invention, and should not be construed as limiting thereof.

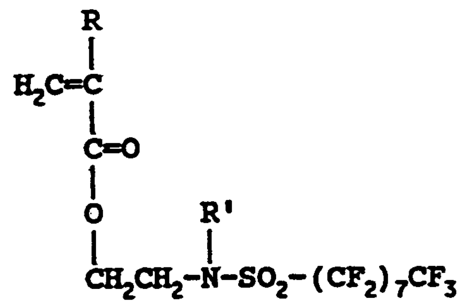
EXAMPLES 1-17

Solubility, Polymerization and Copolymerization of Fluoroacrylate Monomers

EXAMPLE 1

Experimental Procedures

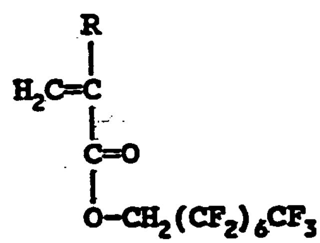
Materials. Five fluoromonomers, illustrated by Formula (II) and Table 1 and Formula (III) and Table 2, were kindly provided by Minnesota Mining and Manufacturing Company (3M). MeFOSEA, EtFOSEA and EtFOSEMA were purified by recrystallization in methanol. 1,1-Dihydroperfluorooctyl acrylate (FOA) was purified by running through Al_2O_3 column to remove the inhibitor. AIBN (Kodak) was recrystallized twice from methanol. Carbon dioxide (Matheson, 99.99%) was passed through copper oxide catalyst column to remove trace amounts of oxygen and then through a molecular sieve(3A) column to remove trace amounts of moisture. Freon-113 ($CF_2ClCFCl_2$) was fractionally distilled before use. Methanol (Mallinckrodt) was used as received.



(II)

Table 1.
Fluorinated Monomers of Formula (II)

Name	R	R'
MeFOSEA	H	CH_3
EtFOSEA	H	CH_2CH_3
MeFOSEMA	CH_3	CH_3
EtFOSEMA	CH_3	CH_2CH_3



(III)

Table 2.
Fluorinated Monomers of Formula (III)

Name	R
FOA	H
FOMA	CH_3

EXAMPLE 2

Comparative Example: Polymerization in Freon 113

Before running polymerizations in supercritical carb n dioxide, a series of poly(perfluoroalkyl acrylate)s and poly(perfluoroalkyl methacrylate)s were prepared using free radical polymerization methods in Freon-113 and in α,α,α-trifluorotoluene and studied their solubility in both liquid and supercritical carbon dioxide. The fluoromonomers employed for this study are those set forth in Tables 1 and 2 above. The polymerization conditions (feed ratios of monomers, initiator and solvents), intrinsic viscosities and molecular weight data are summarized at **Table 3.**

A typical procedure is described below. EtFOSEA (5 g), azobisisobutyronitrile (AIBN) (10 mg) and 10 mL of Freon-113 were put into a 50 mL test tube. After sealing the tube with a rubber septum, the solution was purged with argon for ca. 15 min, placed in a water bath at 60°C and left to polymerize for ca. 20 hours. The tube was opened next day and ca. 30 mL of Freon-113 was added to dilute the polymer solution, followed by precipitation of polymer into methanol. The polymer was filtered and dried in vacuum oven overnight. All of the monomers were polymerized in Freon-113 at 60°C except MeFOSEA which was polymerized in α,α,α-trifluorotoluene at 70°C due to solubility considerations.

Tabl 3

Sample	Feed Ratio monomer (g)	AIBN (mg)	solvent (ml)	[n]	Mw	Mn	MWD
P(EtFOSEA)							
910607-1	2	5	10	0.14	7.68e4	1.13e4	6.79
910607-2	2	10	10	0.11	9.23e4	1.32e4	7.02
910607-3	2	20	10	0.078	7.67e4	2.06e4	3.73
910614-0	3	2+2	2	0.44	1.24e5	5.14e4	2.41
910614-1	5	5	10	0.28	1.14e5	1.39e4	8.20
910614-2	5	10	10	0.28	1.56e5	5.56e4	2.80
910614-3	5	20	10	0.24	1.38e5	5.46e4	2.54
P(EtFOSEMA)							
910710-3	5	5	10	0.13	7.20e4	8.23e3	8.75
P(FOA)							
910710-1	5	5	10	0.21	1.10e6	2.90e5	3.78
P(FOMA)							
910710-2	5	5	10	gel-like			
910711	5	5	20	0.26*	unable to filter		
P(MeFOSEA)**							
910620-1	5	10	20	0.077			
910620-2	5	20	20	0.066			
910620-3	5	30	20	0.010			

All polymerizations are run at 60°C.
* The viscosity of the soluble part.
**Polymerized in , , -trifluorotoluene.

EXAMPLE 3

Solubility Evaluation in Carbon Dioxide

The s lubilities of poly(EtFOSEA) and poly(MeFOSEA) in carbon di xide were measured using a flow system, the results of which are set forth at **Table 4**. Poly(EtFOSEA) was found to be very soluble in both liquid and supercritical carbon dioxide (about 25 wt.%). Poly(MeFOSEA) dissolved in liquid CO_2 at 3000 psi at room temperature. A view cell study discussed below verified that the polymer was also soluble in supercritical CO_2.

For comparison, the solubility of poly(methyl methacrylate) (PMMA) in both liquid and supercritical CO_2 was also studied. Quite differently, PMMA of even lower molecular weight than the two fluoropolymers discussed above is insoluble in carbon dioxide with the pressure ranging from 2000 to 5000 psi and temperature ranging from room temperature to 160°C.

To ensure that the fluoropolymers form homogeneous solutions with carbon dioxide, the solubility of the five fluoropolymers was also determined using a view cell. The results of the observations are set forth at **Table 5**. We observed that all the polymers dissolved and formed clear solutions in carbon dioxide at moderate pressures. Comparatively, poly(FOA) and poly(FOMA) are easier to dissolve in carbon dioxide than poly-(EtFOSEMA), poly(EtFOSEA) and poly(MeFOSEA), but all of the polymers dissolve.

Table 4

Solubility study of F-polymers by flow system:

Sample	[n]	$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	T(°C)	P(psi)	Solubility (wt.%)
P(EtFOSEA)	0.44	1.24	5.14	29	5000	25
P(EtFOSEA)	0.28	1.14	1.39	60	4000	25
P(MeFOSEA)	0.077	—	—	25	3000	15-20
PMMA	—	0.22	1.93	29-160	2000-5000	0

Table 5

Solubility study of F-polymers by view cell:

Sample	[n]	$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	T(°C)	P(psi)	Conc. wt.%vol
P(EtFOSEA)	0.44	1.24	5.14	25	7000	9
P(EtFOSEA)	0.24	1.38	5.46	25	3000	5
P(MeFOSEA)	0.077	—	—	60	3700	5
P(FOA)	0.21	11.0	29.0	25	2000	5
P(FOA)	0.21	11.0	29.0	25	3000	10
P(FOMA)	0.26	—	—	25	2000	5
P(EtFOSEMA)	0.13	0.72	0.82	25	4000	5

* Pressure at which the polymer totally dissolve.

EXAMPLE 4

Polymerization of 1,1-dihydroperfluorooctyl Acrylate (FOA) in Carbon Dioxide

FOA (5.0 g, 11.0 mmol, purified by running through Al_2O_3 column) and AIBN (50 mg, 0.30 mmol, recrystallized twice from methanol) were put into a 10 mL high pressur r action cell with a micromagn tic stir bar inside. The reaction cell was purged with

argon for ca. 10 minutes and then filled with carbon dioxide to a pressure of less than 1000 psi. Over a period of one hour, the cell was heat d to 60°C and the pressure was increased to 3000 psi by th addition of more CO_2. The polymerizati n was continued at these conditions for 48 hours, during which the system was homogeneous and clear.

At the end of the polymerization, carbon dioxide was vented slowly to leave the polymer in the cell. The polymer was dissolved with Freon-113 and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give 3.25 g of transparent viscous polymer (yield: 65%).

Characterizations: ^1H NMR spectrum showed the expected pattern, without vinyl proton peaks of the monomer and without any indication of incorporation of carbon dioxide onto the polymer backbone. The intrinsic viscosity was measured to be 0.19 dL/g in Freon-113 at 30°C. The FTIR spectrum was consistent with the corresponding homopolymer made in Freon-113, with only one carbonyl peak at 1758 cm^{-1}.

EXAMPLE 5

Polymerization of FOA in carbon dioxide

FOA (2.0 g, 4.4 mmol) and AIBN (30 mg, 0.18 mmol) were put into the high pressure cell. Following the same procedure as described in Example 4, polymerization was proceeded at 3000 psi and 60°C for 24 hours, and 0.41 g of polymer was obtained (yield: 21%).

Characterizations: ^1H NMR and FTIR spectra wer consistent with those of the homopolymer made in Freon-113.

EXAMPLE 6

Polymerization of 1,1-dihydroperfluorooctyl Methacrylate (FOMA) in Carbon Dioxide

FOMA (3.0 g, 6.41 mmol, purifi d by running through Al_2O_3 column) and AIBN (30 mg, 0.18 mmol) were put into the 10 mL high pressure reaction cell. The reaction cell was purged with argon for ca. 10 minutes then filled with carbon dioxide to a pressure of less than 1000 psi. Over a period of one hour, the cell was heated to 60°C, and the pressure was increased to 4000 psi by the addition of more CO_2. The polymerization was continued at these conditions for 48 hours, during which the system was homogeneous and clear. At the end of the polymerization, carbon dioxide was vented slowly to leave the polymer in the cell. The polymer was dissolved with Freon-113 and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give 2.19 g of a white powder (yield: 73%).

Characterizations: ^1H NMR and FTIR spectra were consistent with those of the same polymer made in Freon-113. The intrinsic viscosity was measured to be 0.06 dL/g in Freon-113 at 30°C.

EXAMPLE 7

Polymerization of FOMA in CO_2

FOMA (5.0 g, 10.7 mmol) and AIBN (50 mg, 0.3 mmol) was put into the 10 mL high pressure cell. Following the same procedure described in Example 4, the polymerization was carried out in CO_2 at 60°C and 5000 psi for 48 hours. During the entire course of the polymerization, the solution was homogeneous and clear. Th polymer was isolated according to th same procedure as described abov .

Characterizati ns: ^1H NMR and FTIR sp ctra were consistent with those of the same polymer made in

Fr on-113. The intrinsic visc sity was measur d t be 0.06 dL/g in Freon-113 at 30°C.

EXAMPLE 8

Polymerization of 2-(N-methylperfluorooctane-sulfonamido) ethyl Acrylate (MeFOSEA) in Carbon Dioxide

MeFOSEA (5.0 g, 8.75 mmol, purified by recrystallization from methanol) and AIBN (50 mg, 0.30 mmol) were put into the 10 mL high pressure reaction cell. The reaction cell was purged with argon for ca. 10 minutes then filled with carbon dioxide to a pressure of less than 1000 psi. Over a period of one hour the cell was heated to 60°C and the pressure was increased to 5000 psi by the addition of more CO_2. The polymerization was continued at these conditions for 48 hours, during which the system was homogeneous and clear. At the end of the polymerization, carbon dioxide was vented slowly to leave the polymer in the cell. The polymer was dissolved in α,α,α-trifluorotoluene and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give 3.2 g of white powder (yield: 64%).

Characterizations: FTIR spectra were consistent with those of the same polymer made in Freon-113.

EXAMPLE 9

Polymerization of MeFOSEA in Carbon Dioxide

MeFOSEA (1.0 g, 1.75 mmol) and AIBN (10 mg, 0.06 mmol) were put into the high pressure cell. Following the same procedure of Example 4, the p lymerization was proceeded under 4000 psi and 60°C for 8 hours, and 0.19 g f polymer was obtained (yield: 19%).

Characterizations: FTIR spectrum w re consistent with the same polymer made in Fre n-113. The intrinsic viscosity was measured to be 0.064 in α,α,α-trifluorotoluene at 70°C.

EXAMPLE 10

Polymerization of 2-(N-ethylperfluorooctane-sulfonamido) Ethyl Acrylate (EtFOSEA) in Carbon Dioxide

EtFOSEA (5.0 g, 8.53 mmol, purified by recrystallization from methanol) and AIBN (50 mg, 0.30 mmol) were put into the 10 mL high pressure view cell. The reaction cell was purged with argon for ca. 10 minutes then filled with carbon dioxide to a pressure of less than 1000 psi. Over a period of one hour the cell was heated to 60°C and the pressure was increased to 5000 psi by the addition of more CO_2. The polymerization was continued at these conditions for 48 hours, during which the system was homogeneous and clear. At the end of the polymerization, carbon dioxide was vented slowly to leave the polymer in the cell. The polymer was dissolved in Freon-113 and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give 3.9 g of a white powder (yield: 78%).

Characterizations: ^{1}H NMR and FTIR spectra were consistent with those of the same polymer made in Freon-113. The intrinsic viscosity was measured to be 0.20 dL/g in Freon-113 at 30°C. Both the polymers made in CO_2 and in Freon-113 were purified by dissolving in Freon-113 and reprecipitating into methanol and an elemental analysis by ORS was performed. The results are summarized in Table 6 below.

Table 6

Elemental Analysis of Poly(EtFOSEA) Made in Carbon Dioxid and in Freon-113

Sample	% C	% H	% N	% F	% S
P-Freon	28.69	1.86	2.21	51.47	5.05
P-CO_2	28.80	1.91	2.24	50.78	4.81
Calculated	29.01	2.01	2.33	50.64	5.34

EXAMPLE 11

Polymerization of 2-(N-ethylperfluorooctane-sulfonamido) Ethyl Methacrylate (EtFOSEMA) in CO_2

EtFOSEMA (5.0 g, 8.33 mmol, purified by recrystallization from methanol) and AIBN (50 mg, 0.30 mmol) were put into the same reaction vessel. The reaction vessel was purged with argon for ca. 10 minutes then filled with carbon dioxide to a pressure of less than 1000 psi. Over a period of one hour the cell was heated to 60°C, and the pressure was increased to 5000 psi by the addition of more CO_2. The polymerization was continued at these conditions for 48 hours, during which the system was homogeneous and clear. At the end of the polymerization, carbon dioxide was vented slowly to leave the polymer in the vessel. The polymer was dissolved in Freon-113 and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give 3.2 g of white powder.

Characterizati ns: ^{1}H NMR and FTIR sp ctra wer consistent with those f the same polymer made in Fr on-113. The intrinsic viscosity was measured to be 0.10 dL/g in Fr n-113 at 30°C.

EXAMPLE 12

Copolymerization of FOA with Methyl Methacrylat (MMA) in CO_2

FOA (4.0 g, mmol, purified by running through Al_2O_3 column), MMA (1.0 g, 10.0 mmol, purified by vacuum distillation over CaH_2) and AIBN (50 mg, 0.30 mmol) were put into the 10 mL high pressure view cell. The reaction cell was purged with argon for ca. 10 minutes then filled with carbon dioxide to less than 1000 psi. Over a period of one hour the cell was heated to 60°C and the pressure was increased to 5000 psi by the addition of more CO_2. The polymerization was continued at these conditions for 48 hours, during which the system was homogeneous and clear.. At the end of the polymerization, carbon dioxide was vented slowly to leave the polymer in the cell. The polymer was dissolved in Freon-113 and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give 3.25 g of copolymer (yield: 65%). The copolymer was extracted with THF three times to remove any possible PMMA homopolymer.

Characterizations: Solubility of the copolymer in normal solvents and Freon-113 was checked and the results are summarized in Table 7 below.

Table 7

Solubility Test of PFOA-co-PMMA-1

Solvent	solubility
Freon-113	soluble, but slightly cloudy
acetone	liquified but insoluble
THF	liquified but insoluble
CH_2Cl_2	swelled
toluene	swelled
DMF	slightly swelled
DMAc	slightly swelled

^1H NMR and FTIR spectra were indicative of a statistical or random copolymer. Composition of the copolymer was calculated to be 58 mol% FOA from the ^1H NMR spectrum. IR spectrum showed two carbonyl peaks at 1758 (carbonyl of FOA segments) and 1734 cm^{-1} (carbonyl of MMA segments), respectively. The intrinsic viscosity was measured to be 0.10 dL/g in Freon-113 at 30°C.

EXAMPLE 13

Copolymerization of FOA and MMA in Carbon Dioxide

FOA (3.0 g, 6.6 mmol, purified by running through Al_2O_3 column), MMA (2.0 g, 20.0 mmol, purified by vacuum distillation over CaH_2) and AIBN (50 mg, 0.30 mmol) were put into the high pressure cell. The reaction cell was purged with argon for ca. 10 minutes then filled with carbon dioxide to less than 1000 psi. Over a period of one hour the cell was heated to 60°C and the pressure was increased to 5000 psi by the addition of more CO_2. The polymerization system became nonhomogen us aft r ca. 12 hours. After 48 hours, there existed two layers, with the bottom layer accounting for ca. 1/4 of the total reactor volume and a cloudy upper layer accounting for ca. 3/4 of the

total volume. At the end of the polymerization, carbon dioxide was vented slowly t leave the polymer in the cell. The polymer was dissolved in Fre n-113 and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give 3.3 g of copolymer (yield: 66%). The copolymer was extracted with DMF three times.

Characterizations: ^{1}H NMR and FTIR spectra show the expected patterns. Composition of copolymer was calculated from proton NMR spectrum to be 27 mol% in FOA. Two carbonyl peaks appear on the IR spectrum (1758 and 1734 cm^{-1}). The intrinsic viscosity was measured to be 0.12 dL/g in acetone at 30°C. The solubilities of the copolymer in normal solvents are summarized in Table 8 below.

Table 8

Solubility of PFOA-co-PMMA-2 in Different Solvents

Solvent	Solubility
Freon-113	soluble
acetone	soluble
THF	soluble
$CHCl_3$	soluble
CH_2Cl_2	soluble (40 C)
toluene	soluble (100 C)
DMF	insoluble
DMAc	insoluble

Since this copolymer is soluble in normal solvents, ^{13}C NMR and ^{19}F NMR spectra was measured in d6-acetone. Only two carbonyl peaks appeared on the spectrum (177, 178 ppm). The ^{19}F NMR spectrum showed six resonances. GPC was run with THF as s lvent and polystyren as standard. The results were Mn = 5.10×10^4, Mw = 7.45×10^4, MWD = 1.46.

EXAMPLE 14

Copolymerization of FOA and MMA in CO_2 with THF as a Co-Solvent

FOA (3.0 g, 6.6 mmol), MMA (2.0 g, 20 mmol) and AIBN (50 mg, 0.30 mmol) were put into the high pressure cell. 1.0 mL (10 vol%) THF was added into the mixture. The reaction cell was purged with argon for ca. 10 minutes and then filled with carbon dioxide to less than 1000 psi. Over a period of one hour the cell was heated to 60°C, and the pressure was increased to 5000 psi by the addition of more CO_2. The polymerization was continued at these conditions for 48 hours. The system was homogeneous for at least 30 hours at which time it became cloudy. The solution remained homogenous for a longer time than the polymerization reaction conducted without the cosolvent (Example 13). At the end of the polymerization, carbon dioxide was vented slowly to leave the polymer in the cell. The polymer was dissolved in Freon-113 and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give 3.9 g of white polymer (yield: 78%).

Characterizations: GPC was run with THF as solvent. The results were: Mn = 5.50×10^4, Mw = 8.23×10^4, MWD = 1.50.

EXAMPLE 15

Copolymerization of FOA and n-butyl Acrylate (BA) in Carbon Dioxide

FOA (4.0 g, 6.6 mmol), BA (1.0 g, 7.8 mmol, purified by running through Al_2O_3 column) and AIBN (50 mg, 0.30 mmol) wer put into th high pressur reacti n c ll. The reacti n c ll was purged with arg n for ca. 10 minutes then fill d with carbon dioxide t less than 1000 psi. Over a p riod of one hour the cell was

heated to 60°C and the pressure was increased t 5000 psi by the addition of mor CO_2. The polymerization was continued at these conditions for 48 hours, during which the system was homogene us and clear. At the end of the polymerization, carbon dioxide was vented slowly to leave the polymer in the cell. The polymer was dissolved with Freon-113 and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give a transparent elastic material which was purified by extracting with acetone overnight.

Characterizations: ^1H NMR and FTIR spectra were indicative of a random or statistical copolymer. Composition of the copolymer was calculated to be 59% FOA based on ^1H NMR. Two carbonyl resonances appeared in the IR spectrum (1760 and 1720 cm^{-1}). The intrinsic viscosity was 0.45 dL/g in Freon-113 at 30°C. The solubility of the copolymer is summarized in Table 9.

Table 9

The Solubility of PFOA-co-PBA in Different Solvents

Solvent	Solubility
Freon-113	soluble
acetone	insoluble
THF	insoluble
$CHCl_3$	dispersed but insoluble
toluene	insoluble
DMF	insoluble

EXAMPLE 16

__Copolymerization of FOA with Styrene in CO_2__

FOA (4.0 g, 6.6 mmol), styren (1.0 g, 9.6 mmol, purified by vacuum distillation) and AIBN (50 mg,

0.30 mmol) wer put int the high pressur reaction cell. The reaction cell was purged with arg n f r ca. 10 minut s then filled with carbon dioxide to less than 1000 psi. Over a period of one hour the cell was heated to 60°C and the pressure was increased to 5000 psi by the addition of more CO_2. The polymerization was continued at these conditions for 48 hours, during which the system was homogeneous and clear. At the end of the polymerization, carbon dioxide was vented slowly to leave the polymer in the cell. The polymer was dissolved with Freon-113 and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give a very tacky material. The polymer was extracted with acetone overnight to remove any possible styrene homopolymer.

Characterizations: ^1H NMR and FTIR spectra were indicative of a random or statistical copolymer. All the peaks of FOA were shifted upfield by ca. 0.4 ppm. Also the peak of the methylene proton adjacent to the perfluoroalkyl chain was broadened. IR spectrum showed one carbonyl resonance at 1758 cm^{-1} and peaks appeared in the region between 3000 to 3100 cm^{-1} due to the stretching vibration of C-H on the phenyl ring of the styrene repeating unit.

EXAMPLE 17

Copolymerization of FOA with Ethylene in CO_2

FOA (4.0 g, 6.6 mmol) and AIBN (50 mg, 0.30 mmol) were put into the high pressure cell. Ethylene (0.46 g, 16.4 mmol) was transferred from a small bomb into the reaction cell. CO_2 was added, and the temperature was raised to 60°C and the total pressure was 5000 psi. The polym rization was allowed to proceed f r ca. 48 h urs. During this time period, the system remained homogeneous and clear. Aft r venting CO_2, the product was dissolved with Freon-113 and

pr cipitated into large excess of methanol t give 2.9 g of viscous polymer (yield: 65%). The cop lymer was extracted with boiling toluene f r two hours to remove any polyethylene homopolymer.

Characterization: The copolymer was insoluble in acetone, toluene, THF, chloroform and DMF. It was soluble in Freon-113. ^1H NMR spectrum showed a new peak appearing at ca. 1.5 ppm, which is presumably due to the protons of the ethylene repeat unit. FTIR show similar pattern to PFOA homopolymer. The resonance of ethylene repeat unit may be buried by the resonance of the backbone of FOA. Intrinsic viscosity was measured to be 0.14 dL/g in Freon-113 at 30°C.

EXAMPLE 18

Cationic Polymerization of Vinyl Ethers in CO_2

Vinyl ethers with a fluoroalkyl group according to Formula (IV):

$$R^1R^2C{=}CR^3O(CH_2)_nR \qquad \text{(IV)}$$

wherein:

n is 0, 1, or 2;

R^1, R^2, and R^3 are each independently hydrogen or fluorine; and

R is perfluorinated aliphatic or perfluorinated aromatic group,

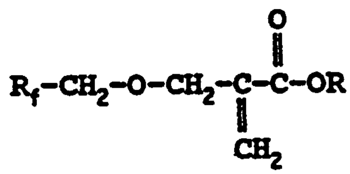
for example, $CH_2{=}CH{-}OCH_2CH_2N(n{-}C_3H_7)SO_2C_8F_{17}$ or $CH_2{=}CH{-}OCH_2C_8F_{17}$, are polymerized with an initiator such as boron trifluoroetherate, hydrogen iodine/iodine, and hydrogen iodine/zinc iodine in liquid and supercritical carbon dioxide using the procedure of Example 4 above. It has previously been known that these monomers could be solvent polymerized in Freon. *Se* W. Choi et al., *Polymer J.* **20**, 201 (1988). Thus, this exampl indicates that the ability f a monomer to undergo solution polymerization in Freon-113 is a good

indicat r that the mon mer can be polym rized in liquid or supercritical carbon dioxid .

EXAMPLE 19

Polymerization of 1,1-Disubstituted Monomers

1,1-disubstituted monomers according to Formula (V):



(V)

wherein R is C1-C4 alkyl (e.g., ethyl) and R_f is $(CF_2)_nF$ wherein n is 1-10, (e.g., CF_3, $(CF_2)_2F$, $(CF_2)_7F$, or $(CF_2)_{10}F$), are polymerized in liquid or supercritical carbon dioxide under conditions using the procedure of Example 4 above.

EXAMPLE 20

Polymerization with Chain Transfer Agents

Functional fluoropolymers are produced in liquid or supercritical carbon dioxide by polymerizing a fluoromonomer such as FOA in carbon dioxide in the presence of a chain transfer agent such as substituted allylic sulfides. This results in fluoropolymers capped with a carboxy, hydroxy, trialkylsilyl, or amino groups.

EXAMPLE 21

Polymerization of Block Fluoropolymers

Block fluoropolymers are produced in liquid or supercritical carbon dioxide using the procedure of Example 4 above, using pseudo-living free radical polymerization routes. For exampl , FOA is polym rized in carbon dioxide with nitroxides similar to that discl sed in U.S. Pat nt No. 4,581,429 or with oxygen-

centered radical species generated from hyponitrite, arenediazoate, or cyanate anions by reaction with electron acceptors such as arenediazonium ions or activated alkyl halides with sequential monomer additions, similar to Druliner, J.D., *Macromolecules* 1991, 24, 6079.

EXAMPLE 22

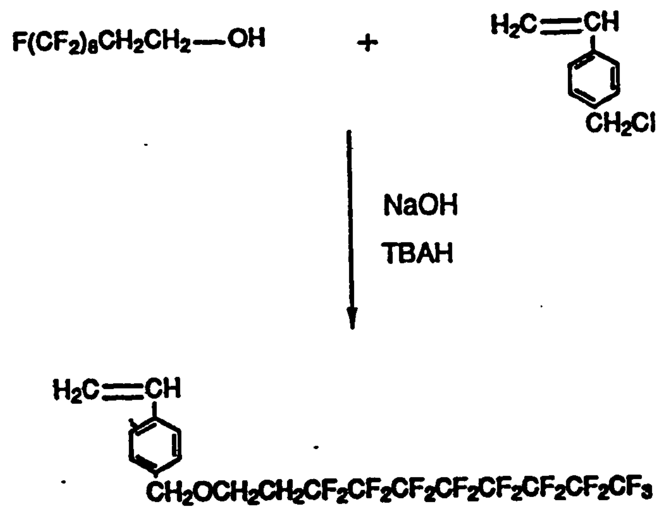
Poly(perfluoroalkyl ether) Polymerization

Poly(perfluoroalkyl ether)s are made in liquid or supercritical carbon dioxide using the procedure of Example 4 above. For example, perfluoropropylene oxide is polymerized using initiators derived from alkali metal fluorides and an acid fluoride such as CF_3CO-F in carbon dioxide to yield viscous oils.

EXAMPLE 23

Preparation of Monomers

Styrene (Aldrich), methyl methacrylate (MMA) (Aldrich), acrylic acid (AA) (Aldrich) were purified by running through an alumina column and deoxygenated before polymerization. N-Octyl acrylate (OA), octadecyl methacrylate (ODMA) and all the perfluoroalkyl acrylates described above in Example 1 were purified in a similar fashion. Vinylidene fluoride (VF_2) (Aldrich, 99+%) and pentafluorostyrene (5FSt) (PCR Inc.) were used as received. The styrene-based monomer carrying a fluorocarbon segment, *p*-perfluoroalkylethyleneoxymethyl styrene (STF), was prepared by a phase-transfer-catalyzed etherification of fluorocarbon-substituted alcohol with *p*-(chloromethyl) styrene:



EXAMPLE 24

Homopolymerization of Fluorostyrene Monomer
<u>*p-perfluoroalkylethyleneoxymethyl Styrene (STF)*</u>

A typical example of a homopolymerization in supercritical CO_2 was conducted as follows. STF (1.0 g, 1.72 mmol) and AIBN (30 mg, recrystallized twice from methanol) were put into a 10-mL high pressure view cell containing a micromagnetic stir bar. The reaction cell was purged with argon for ca. 10 minutes, and then filled with CO_2 to less than 68 bar. The cell was heated to 60°C and the pressure was increased to 345 bar by the addition of more CO_2. The polymerization was continued at these conditions for 3 days, during which time the system remained homogeneous and optically transparent. At the end of the polymerization, the cell was cooled to room temperature and CO_2 was vented resulting in the precipitation of the polymer. The unreacted monomer was extracted with dichloromethane. The polymer was dried to constant weight and characterized (65% yield).

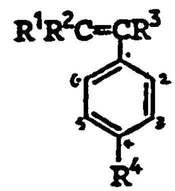
The other monomers (VF_2, 5FSt, styren , MMA, AA) w re all homopolym riz d in supercritical carbon dioxide according to a procedur similar to that above;

however, these polymers precipitated during the course of the reaction in CO_2 under the conditions described.

EXAMPLE 25

Homopolymerization of Fluorostyrene Monomer

Fluorostyrene monomers according to Formula (VI):



(VI)

wherein:

R^1 and R^2 are each independently hydrogen, fluorine, or methyl;

R^3 is hydrogen, fluorine, methyl or perfluoromethyl;

R^4 is hydrogen, fluorine, or C1-C12 perfluorinated aliphatic group; and

the 2, 3, 5, and 6 positions of the aromatic styrene ring are each independently hydrogen or fluorine, are polymerized with an initiator such as AIBN in liquid and supercritical carbon dioxide using the concentrations and procedure of Example 24 above.

EXAMPLE 26

Copolymerization of Fluorinated Monomer (Fluoroacrylate MeFOSEA) with Non-Fluorinated Comonomer (OA)

A copolymerization of the fluorinated monomers with non-fluorinated monomers in supercritical CO_2 was conducted as follows. 2-(N-Methylperfluoro-octanesulfonamido) ethyl acrylate (MeFOSEA, 1.3 g, 2.12 mmol), OA (0.70 g, 3.80 mmol) and AIBN (30 mg, 0.18 mmol) were put into the 10-mL high pressure view cell. F llowing the procedure as described above in Example 24, the cop lymerization was continued at 60°C and 345 bar for 24 hours. The system was homogeneous during the entire course of the polymerizati n. After venting

th CO_2, the copolym r was rediss lved in Fr on-113 and precipitated into larg excess f methanol. The polymer was filter d and washed with m thanol several times and dried in vacu overnight t give 1.35 g of copolymer (68% yield).

The other non-fluorinated monomers are also copolymerized in a similar fashion.

EXAMPLE 27

Copolymerization of Fluorinated Monomer (Fluoroacrylate FOA) With Fluorinated Comonomer (Vinylidene Fluoride)

The 10-mL high pressure cell was loaded with 1,1-dihydroperfluorooctyl acrylate (FOA, 3.0 g, 6.6 mmol) and AIBN (50 mg, 0.30 mmol). After purging with argon thoroughly, the cell was connected to a VF_2 cylinder, 3.02 of VF_2 (47.2 mmol) was transferred into the cell by cooling down the cell in a dry ice/isopropanol bath. After warming the cell to room temperature, carbon dioxide was filled to ca. 68 bar. The heating of the cell was continued and more CO_2 was added until the cell reached 60°C and 345 bar. The polymerization was continued at these conditions for ca. 50 hours during which the system was homogeneous during the entire course of the reaction. The copolymer was obtained according to the same work-up procedure.

EXAMPLE 28

Polymerization of 1,1-difluoroethylene (VF_2)

A low molecular weight polymer or oligomer was made in carbon dioxide by polymerizing 1,1-difluoroethylene (VF_2) in the presence of a perfluoroalkyliodide. 1.0 g of C_4F_9I and 2.0 g of VF_2 was transferred into a 10-mL stainless ste 1 cell fitted with sapphir windows. The cell was heated to 36°C and filled to 3000 psi with carb n dioxid . The reaction was homogen ous (optically transparent and

c lorless). The cell was irradiated with an ultravi let lamp for 24 hours, during which time the reaction remained homogen ous and turned c lor from c lorless t light purple or pink.

$$\underbrace{CF_3CF_2CF_2CF_2}_{R_f}{-}I \quad + \quad H_2C{=}CF_2$$

$$\Big\downarrow \text{UV irradiation, 24 hrs, Carbon dioxide, 36 °C, 3000 psi}$$

$$R_f{-}CH_2CF_2I$$
$$R_f{-}CF_2CH_2I$$

$$R_f{-}CH_2CF_2CH_2CF_2I$$
$$R_f{-}CH_2CF_2CF_2CH_2I$$
$$R_f{-}CF_2CH_2CH_2CF_2I$$
$$R_f{-}CF_2CH_2CF_2CH_2I$$

$$R_f{-}CH_2CF_2CH_2CF_2CH_2CF_2I$$

The product distribution was determined by gas chromatography-mass spectrometry to include the various products listed above with the various regioisomers as shown.

EXAMPLE 29

A low molecular weight polymer or oligomer is made in carbon dioxide by polymerizing tetrafluoroethylene (TFE) using the concentrations and procedures of Example 28 above, but in the presence of a chain transfer agent such as trifluoromethyl iodide or IF to yield:

$$CF_3{-}\left(CF_2CF_2\right)_n{-}I$$

or

$$F{-}\left(CF_2CF_2\right)_n{-}I$$

under h mogene us conditions in a stainless steel or Hastalloy reactor/view cell.

EXAMPLE 30

Following the procedure set forth in Example 28 and 29 above, fluoroolefins, such as tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), perfluoro-2,2-dimethyl-1,3-dioxole or mixtures of these monomers, or with the addition of ethylene monomer, are polymerized under homogeneous conditions in carbon dioxide.

EXAMPLE 31

Low molecular weight polymers or oligomers are made in carbon dioxide using a process essentially as described in Examples 28, 29 and 30 above, but the reaction product is endcapped with ethylene to yield:

$$CF_3\left(CF_2CF_2\right)_n CH_2CH_2-I$$

or

$$F\left(CF_2CF_2\right)_n CH_2CH_2-I$$

EXAMPLE 32

A dimer, oligomer or low molecular weight polymer of CTFE, HFP, TFE, or VF_2 is obtained by following the procedures of Example 28 above, except that the fluoroolefin or mixtures of the fluoroolefins are treated with I_2 or another Lewis acid (such as $FeCl_3$) in carbon dioxide to form a product soluble in carbon dioxide. Halogenated chain transfer agents or telogens such as Cl_3CBr, $CFCl_3$, $CFCl_3$, CCl_4, Br-CFCl-CF_2-Br are optionally added. The reactions are optionally facilitat d by UV irradiation r added peroxide.

EXAMPLE 33

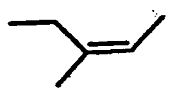
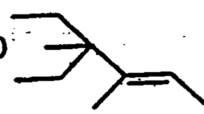
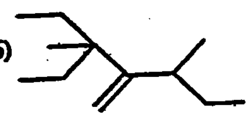
Terpolymerization of Fluoroolefin Monomers

A flu ropolymer is made by terp lymerizing TFE, CTFE, and ethylene in carbon dioxide using a peroxide initiator and a chain transfer agent such as freon-11 and the following ratios of TFE/CTFE/Ethylene: 20/45/35; 10/55/35; and 30/30/40.

EXAMPLE 34

Polymerization of Fluoroolefin TFE

An oligomer or low molecular weight polymer of TFE is made in carbon dioxide by treating TFE with a nucleophile in carbon dioxide oxide to form a carbon dioxide-soluble product, such as trimer, tetramer, pentamer and hexamer.

(3)  (4)  (5)  (6) 

EXAMPLE 35

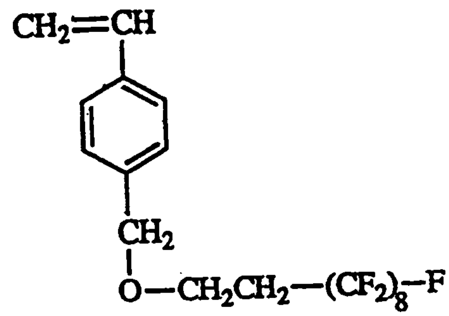
Polymerization of Fluoroolefin HFP

An oligomer or low molecular weight polymer of hexafluoropropylene (HFP) is obtained by treating HFP with a nucleophile such as CsF in carbon dioxide to form a soluble product in carbon dioxide.

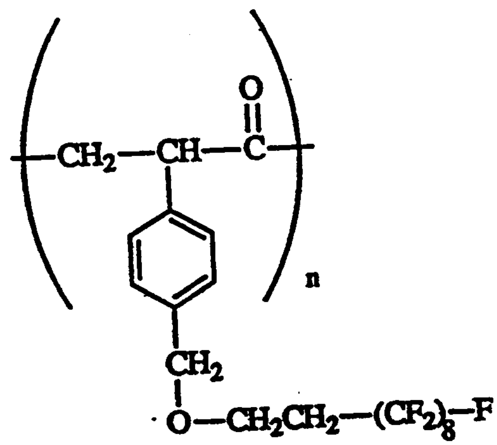
EXAMPLE 36

Polymerization of Fluorostyrene Monomer STF Using a Palladium Catalyst

A polymer is made in carbon dioxide under the homogeneous conditions by copolymerizing a fluorinated monomer, such as:



with carbon monoxide using a palladium catalyst (for concentrations, see, e.g., M. Brookhart et al., J. Am. Chem. Soc. 114, pg. 5894 (1992)) to yield:



EXAMPLE 37

Polymerization Using a Cosolvent

A polymerization is carried out in essentially the same manner as described above, except that a cosolvent is added to carbon dioxide, such as less than about 5% by weight diglyme, to form a product soluble in carbon dioxide.

EXAMPLE 38

Isolation of Polymer

A process is carried out in essentially the same manner as described in Exampl s 23-37 above, exc pt that the product is is lat d ither all at once by continuous reduction of pressure (venting) r is

is lated in fractions by controlled release or step-wise reduction of pressure and subs quent c llecti n and separation of the product.

EXAMPLE 39

Solubility of Fluoroolefin Polymer TFE

A low molecular weight polymer or oligomer of tetrafluoroethylene (TFE) with the structure:

$$F\left(CF_2CF_2\right)_n I$$

where n = 1-5, was completely dissolved in carbon dioxide at 5000 psi and 60°C.

EXAMPLE 40

Solubility of Endcapped Fluoroolefin Polymer TFE

A low molecular weight polymer or oligomer of TFE which was endcapped with ethylene, having the structure:

$$F\left(CF_2CF_2\right)_n CH_2CH_2 - I$$

where n = 1-5, was dissolved in carbon dioxide at 2000 psi and 60°C.

EXAMPLE 41

Solubility of Fluoroolefin Polymer CTFE

A low molecular weight polymer or oligomer of chlorotrifluoroethylene (CTFE) with the structure:

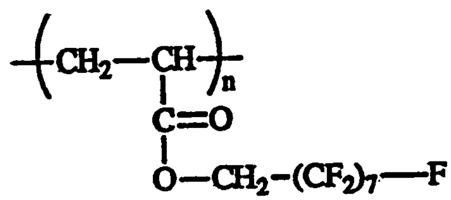
$$F\left(CF_2CFCl\right)_n F$$

was dissolved in carbon di xid over a wide range of pressur s and weight fracti ns. The phase diagram at 40°C as shown in Figure 1 was det rmin d.

EXAMPLE 42

Solubility of Fluoroacrylate Polymer FOA

A high molecular weight polymer of (1,1-dihydroperfluorooctyl) acrylate with the structure:

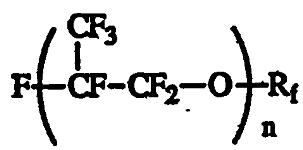


was dissolved in carbon dioxide over a wide range of pressures and weight fractions. The phase diagram at 60°C as shown in Figure 2 was determined.

EXAMPLE 43

Solubility of Fluoroalkylene Oxide Polymer

A low molecular weight polymer or oligomer of hexafluoropropylene oxide (Krytox) with the structure:

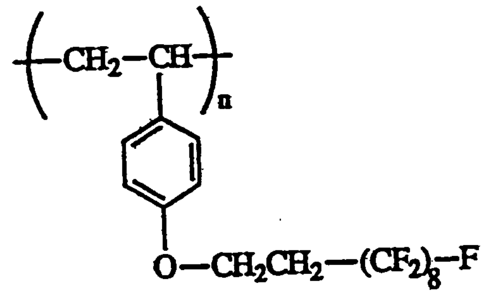


was dissolved in carbon dioxide at 5000 psi and 60°C.

EXAMPLE 44

Solubility of Fluorostyrene Polymer

A high molecular weight polymer of a fluoroalkysubstituted styrene monomer with the structure:

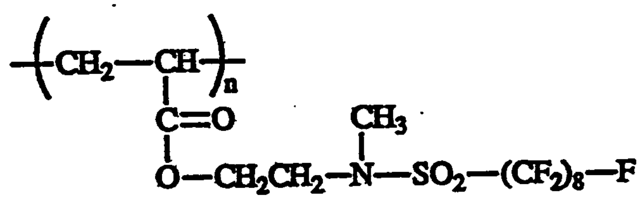


was dissolved in carbon dioxide at 5000 psi and 60°C.

EXAMPLE 45

Solubility of Fluoroacrylate Polymer MeFOSEA

A high molecular weight polymer with the structure:

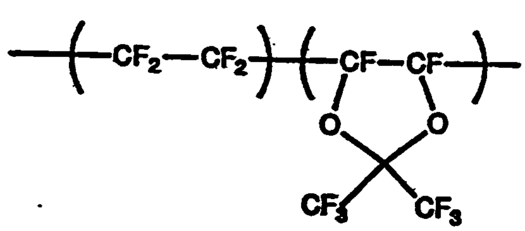


was dissolved in carbon dioxide at 5000 psi and 60°C.

EXAMPLE 46

Solubility of Fluoroolefin-Teflon Copolymer

A high molecular weight statistical copolymer of TFE and perfluoro-2,2-dimethyl-1,3-dioxole (Teflon AF 1600) having the following structure:



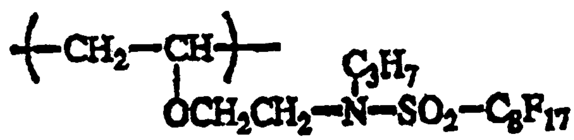
was heated to 80°C and pressurized to 6000 psi with carbon di xide. At these conditions two liquid phases f rmed – a polymer rich phase and a carbon dioxide rich phase. Upon venting, the carbon di xide-rich phase

turned cloudy indicating that some of th polymer diss lv d in carbon dioxide.

EXAMPLE 47

Solubility of Fluorinated Vinyl Ether Polymer

A high molecular weight polymer with the structure:



was dissolved in carbon dioxide at 3490 psi at 60°C. The polymer also dissolves in freon-113, but is insoluble in common organic solvents such as THF, dichloromethane, and chloroform.

The foregoing examples are illustrative of the present invention, and are not to be taken as restrictive thereof. The invention is defined by the following claims, with equivalents of the claims to be included therein.

THAT WHICH IS CLAIMED IS:

1. A process f r making a flu ropolym r, comprising:

s lubilizing a fluoromonomer selected from the group consisting of fluoroacrylate monomers, fluoroolefin monomers, fluorostyrene monomers, fluorinated vinyl ether monomers, and fluoroalkylene oxide monomers in a solvent, the solvent comprising carbon dioxide fluid; and then

polymerizing the fluoromonomer in said solvent to produce said fluoropolymer.

2. A process according to claim 1, wherein said carbon dioxide fluid is liquid carbon dioxide.

3. A process according to claim 1, wherein said carbon dioxide fluid is supercritical carbon dioxide.

4. A process according to claim 1, further comprising the step of separating said fluoropolymer from said carbon dioxide and collecting said fluoropolymer.

5. A process according to claim 4, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

6. A process according to claim 1, further comprising:

solubilizing a comonomer in said carbon dioxide fluid,

and wherein said polymerizing step comprises copolymerizing said fluoromonomer with said comonomer.

7. A process according to claim 1, wherein said polymerizing step is carried ut in the presence of an initiator.

8. A process according to claim 1, wherein said solvent further comprises a cosolvent.

9. A process according to claim 1, wherein said polymerizing step is carried out in the presence of a chain transfer agent.

10. A process for making a fluoroacrylate polymer, comprising:

solubilizing a fluoroacrylate monomer in a solvent, the solvent comprising carbon dioxide fluid; and then

polymerizing the fluoroacrylate monomer in said solvent to produce said fluoroacrylate polymer.

11. A process according to claim 10, wherein said carbon dioxide fluid is liquid carbon dioxide.

12. A process according to claim 10, wherein said carbon dioxide fluid is supercritical carbon dioxide.

13. A process according to claim 10, further comprising the step of separating said fluoropolymer from said carbon dioxide and collecting said fluoropolymer.

14. A process according to claim 13, wherein said s parating step is carried out by venting said carbon dioxide to th atmosph r .

15. A process according to claim 10, further comprising:

solubilizing a com nomer in said carbon dioxide fluid,

and wherein said polymerizing step comprises copolymerizing said fluoromonomer with said comonomer.

16. A process according to claim 10, wherein said polymerizing step is carried out in the presence of an initiator.

17. A process according to claim 10, wherein said solvent further comprises a cosolvent.

18. A process according to claim 10, wherein said polymerizing step is carried out in the presence of a chain transfer agent.

19. A process for making a fluoroacrylate polymer, comprising:

solubilizing a fluoroacrylate monomer in a solvent, the solvent comprising carbon dioxide fluid wherein said fluoroacrylate monomer comprises a monomer of formula (I):

$$H_2C{=}CR^1COO(CH_2)_nR^2 \qquad \text{(I)}$$

wherein:

n is 1 or 2;

R^1 is hydrogen or methyl; and

R^2 is a perfluorinated aliphatic or perfluorinated aromatic group; and then

polymerizing the fluoroacrylate monomer in said solvent to produce said flu roacrylate polymer.

20. A pr cess acc rding to claim 19, wherein R^2 is a C1 t C8 perfluoroalkyl or $-CH_2NR^3SO_2R^4$, wher in R^3 is C1-C2 alkyl and R^4 is C1 t C8 perflu r alkyl.

21. A process according to claim 19, wherein said fluoroacrylate monomer is selected from the group consisting of:

2-(N-ethylperfluorooctanesulfonamido) ethyl acrylate;

2-(N-ethylperflooctanesulfonamido) ethyl methacrylate;

2-(N-methylperfluorooctanesulfonamido) ethyl acrylate;

2-(N-methylperflooctanesulfonamido) ethyl methacrylate;

1,1-Dihydroperfluorooctyl acrylate; and

1,1-Dihydroperfluorooctyl methacrylate.

22. A process according to claim 19, wherein said carbon dioxide fluid is liquid carbon dioxide.

23. A process according to claim 19, wherein said carbon dioxide fluid is supercritical carbon dioxide.

24. A process according to claim 19, further comprising the step of separating said fluoropolymer from said carbon dioxide and collecting said fluoropolymer.

25. A process according to claim 24, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

26. A process according to claim 19, further comprising:

solubilizing a comonomer in said carbon dioxide fluid,

and wherein said polymerizing step comprises copolymerizing said fluoromonomer with said comonomer.

27. A process according to claim 19, wherein said polymerizing step is carried out in the presence of an initiator.

28. A process according to claim 19, wherein said solvent further comprises a cosolvent.

29. A process according to claim 19, wherein said polymerizing step is carried out in the presence of a chain transfer agent.

30. A process for making a fluoroalkylene oxide polymer, comprising:

solubilizing a fluoroalkylene oxide monomer in a solvent comprising carbon dioxide fluid; and then

polymerizing the fluoroalkylene oxide monomer in said solvent to produce said fluoroalkylene oxide polymer.

31. A process according to Claim 30 wherein said fluoroalkylene oxide monomer is selected from the group consisting of perfluoropropylene oxide and perfluorocyclohexene oxide.

32. A process according to claim 30, wherein said carbon dioxide fluid is liquid carbon dioxide.

33. A proc ss according to claim 30, wherein said carbon dioxide fluid is supercritical carbon di xide.

34. A proc ss acc rding to claim 30, further comprising the step of separating said flu roalkylene xide polymer from said carbon dioxide and collecting said flu roalkylene oxide p lymer.

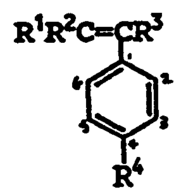
35. A process according to claim 35, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

36. A process for making a fluorostyrene polymer, comprising:

solubilizing a fluorostyrene monomer in a solvent comprising carbon dioxide fluid; and then

polymerizing the fluorostyrene monomer in said solvent to produce said fluorostyrene polymer.

37. A process according to Claim 36, wherein said fluorostyrene monomer comprises a monomer of Formula (VI):



(VI)

wherein:

R^1 and R^2 are each independently hydrogen, fluorine, or methyl;

R^3 is hydrogen, fluorine, methyl or perfluoromethyl;

R^4 is hydrogen, fluorine, or C1-C12 perfluorinated aliphatic group; and

wherein the 2, 3, 5, and 6 positions of the aromatic styrene ring are each independently hydrogen or flu rin .

38. A process acc rding to claim 36, wherein said carb n dioxide fluid is liquid carbon di xide.

39. A process acc rding to claim 36, wherein said carbon dioxide fluid is supercritical carbon dioxide.

40. A process according to claim 36, further comprising the step of separating said fluorostyrene polymer from said carbon dioxide and collecting said fluorostyrene polymer.

41. A process according to claim 40, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

42. A process for making a fluorinated vinyl ether polymer comprising:

solubilizing a fluorinated vinyl ether monomer in a solvent comprising carbon dioxide fluid; and then

polymerizing the fluorinated vinyl ether monomer in said solvent to produce said fluorinated vinyl ether polymer.

43. A process according to Claim 42, wherein said fluorinated vinyl ether monomer comprises a monomer of Formula (IV):

$$R^1R^2C{=}CR^3O(CH_2)_nR \qquad \text{(IV)}$$

wherein:

n is 0, 1 or 2;

R^1, R^2, and R^3 are each independently hydrogen r fluorine; and

R is p rfluorinated aliphatic or perfluorinated aromatic group.

44. A process according to claim 42, wherein said carbon dioxide fluid is liquid carbon dioxide.

45. A process according to claim 42, wherein said carbon dioxide fluid is supercritical carbon dioxide.

46. A process according to claim 42, further comprising the step of separating said fluorinated vinyl ether polymer from said carbon dioxide and collecting said fluorinated vinyl ether polymer.

47. A process according to claim 46, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

48. A process for making a fluoroolefin polymer comprising:

solubilizing a fluoroolefin monomer in a solvent comprising carbon dioxide fluid; and then

polymerizing the fluoroolefin monomer in said solvent to produce said fluoroolefin polymer.

49. A process according to Claim 48 wherein said fluoroolefin monomer is selected from the group consisting of difluoroethylene, tetrafluoroethylene, hexafluoropropylene, chlorotrifluoroethylene, perfluoro-2,2-dimethyl-1,3-dioxole and mixtures thereof.

50. A process according to claim 48, wherein said carbon dioxide fluid is liquid carbon dioxide.

51. A process according to claim 48, wherein said carbon dioxide fluid is supercritical carbon dioxide.

52. A process according to claim 48, further comprising the step of separating said fluor olefin polymer from said carb n di xide and c ll cting said fluoroolefin polymer.

53. A process according to claim 52, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

AMENDED CLAIMS

[received by the International Bureau on 13 September 1993 (13.09.93); original claims 1-53 replaced by amended claims 1-26 (6 pages)]

1. A pr cess for making a fluoropolymer, comprising:

solubilizing a fluoromonomer selected from th group consisting of fluoroacrylate monomers, fluoroolefin monomers, fluorostyrene monomers, fluorinated vinyl ether monomers, and fluoroalkylene oxide monomers in a solvent, the solvent comprising carbon dioxide fluid; and then

polymerizing the fluoromonomer in said solvent to produce said fluoropolymer;

wherein said polymerizing step is a solution polymerization step.

2. A process according to claim 1, wherein said polymerizing step is carried out in the presence of a chain transfer agent.

3. A process for making a fluoroacrylate polymer, comprising:

solubilizing a fluoroacrylate monomer in a solvent, the solvent comprising carbon dioxide fluid; and then

polymerizing the fluoroacrylate monomer in said solvent to produce said fluoroacrylate polymer.

4. A process according to claim 3, wherein said polymerizing step is carried out in the presence of a chain transfer agent.

5. A process for making a fluoroacrylate polymer, comprising:

solubilizing a fluoroacrylate monomer in a solvent, the solvent comprising carbon dioxide fluid wherein said fluoroacrylate m nomer comprises a monomer of formula (I):

$$H_2C{=}CR^1COO(CH_2)_nR^2 \qquad (I)$$

Wherein:

n is 1 or 2;

R^1 is hydrogen or methyl; and

R^2 is a perfluorinated aliphatic or perfluorinated aromatic group; and then

polymerizing the fluoroacrylate monomer in said solvent to produce said fluoroacrylate polymer.

6. A process according to claim 5, wherein R^2 is a C1 to C8 perfluoroalkyl or $-CH_2NR^3SO_2R^4$, wherein R^3 is C1-C2 alkyl and R^4 is C1 to C8 perfluoroalkyl.

7. A process according to claim 5, wherein said fluoroacrylate monomer is selected from the group consisting of:

2-(N-ethylperfluorooctanesulfonamido) ethyl acrylate;

2-(N-ethylperflooctanesulfonamido) ethyl methacrylate;

2-(N-methylperfluorooctanesulfonamido) ethyl acrylate;

2-(N-methylperflooctanesulfonamido) ethyl methacrylate;

1,1-Dihydroperfluorooctyl acrylate; and

1,1-Dihydroperfluorooctyl methacrylate.

8. A process according to claim 5, wherein said polymerizing step is carried out in the presence of a chain transfer agent.

9. A proc ss for making a fluoroalkylene oxide polymer, comprising:

solubilizing a flu roalkylene oxid monomer in a solvent comprising carbon dioxide fluid; and then

polymerizing the fluoroalkylene oxide monomer in said solvent to produce said fluoroalkylene oxide polymer.

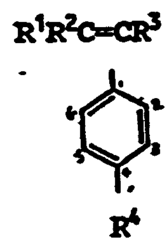
10. A process according to Claim 9 wherein said fluoroalkylene oxide monomer is selected from the group consisting of perfluoropropylene oxide and perfluorocyclohexene oxide.

11. A process for making a fluorostyrene polymer, comprising:

solubilizing a fluorostyrene monomer in a solvent comprising carbon dioxide fluid; and then

polymerizing the fluorostyrene monomer in said solvent to produce said fluorostyrene polymer.

12. A process according to Claim 11, wherein said fluorostyrene monomer comprises a monomer of Formula (VI):



(VI)

wherein:

R^1 and R^2 are each independently hydrogen, fluorine, or methyl;

R^3 is hydrogen, fluorine, methyl or perfluoromethyl;

R^4 is hydrogen, fluorin , r C1-C12 perfluorinated aliphatic group; and

wherein the 2, 3, 5, and 6 positions of the aromatic styrene ring are each independently hydrogen or fluorine.

13. A process for making a flu rinat d vinyl ether polymer comprising:

solubilizing a fluorinated vinyl ether monomer in a solvent comprising carbon dioxide fluid; and then

polymerizing the fluorinated vinyl ether monomer in said solvent to produce said fluorinated vinyl ether polymer.

14. A process according to Claim 13, wherein said fluorinated vinyl ether monomer comprises a monomer of Formula (IV):

$$R^1R^2C{=}CR^3O(CH_2)_nR \qquad (IV)$$

wherein:

n is 0, 1 or 2;

R^1, R^2, and R^3 are each independently hydrogen or fluorine; and

R is perfluorinated aliphatic or perfluorinated aromatic group.

15. A process for making a fluoroolefin polymer comprising:

solubilizing a fluoroolefin monomer in a solvent comprising carbon dioxide fluid; and then

polymerizing the fluoroolefin monomer in said solvent to produce said fluoroolefin polymer;

wherein said polymerizing step is a solution polymerization step.

16. A process according to Claim 15, wherein said fluoroolefin m nomer is selected from th group consisting f diflu roethylene, tetrafluoroethylene, hexafluoropropylen , chlorotrifluoro thylene,

perfluor -2,2-dimethyl-1,3-diox le and mixtures there f.

17. A process according to claim 15, wherein said polymerizing step is carried out in the presence of a chain transfer agent.

18. A process according to claim 15, wherein said fluoroolefin polymer is an amorphous tetrafluoroethylene copolymer.

19. A process according to claim 15, wherein said fluoroolefin polymer is an amorphous fluoroolefin polymer which is a fluorocarbon elastomer.

20. A process according to claim 1, 3, 5, 9, 11, 13, or 15, wherein said carbon dioxide fluid is liquid carbon dioxide.

21. A process according to claim 1, 3, 5, 9, 11, 13, or 15, wherein said carbon dioxide fluid is supercritical carbon dioxide.

22. A process according to claim 1, 3, 5, 9, 11, 13, or 15, further comprising the step of separating said polymer from said carbon dioxide and collecting said polymer.

23. A process according to claim 19, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

24. A process according to claim 1, 3, 5, 9, 11, 13, or 15, further comprising:

solubilizing a comonomer in said carbon dioxide fluid,

and wherein said polymerizing step comprises copolymerizing said fluoromonomer with said comonomer.

25. A process according to claim 1, 3, 5, 9, 11, 13, or 15, wherein said polymerizing step is carried out in the presence of an initiator.

26. A process according to claim 1, 3, 5, 9, 11, 13, or 15, wherein said solvent further comprises a cosolvent.

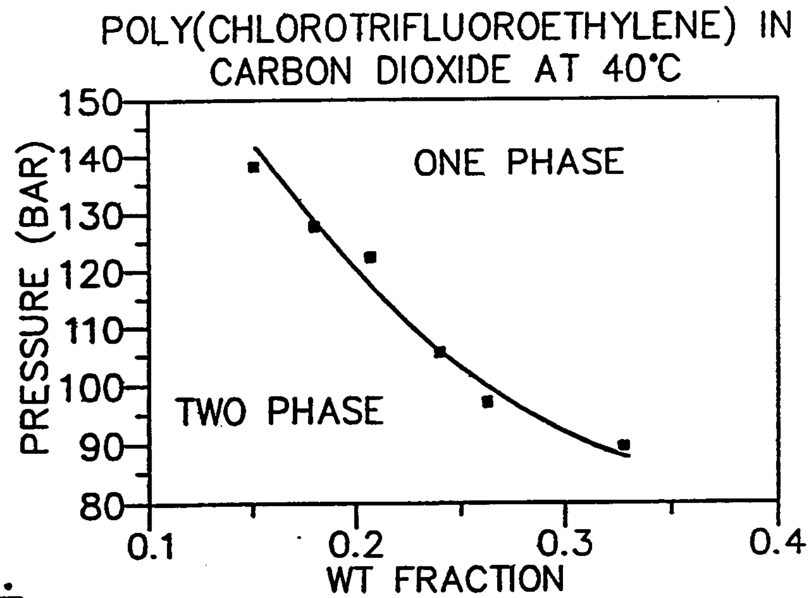

POLY(CHLOROTRIFLUOROETHYLENE) IN CARBON DIOXIDE AT 40°C
PRESSURE (BAR)
150
140
130
120
110
100
90
80
ONE PHASE
TWO PHASE
0.1
0.2
0.3
0.4
WT FRACTION

FIG. 1.

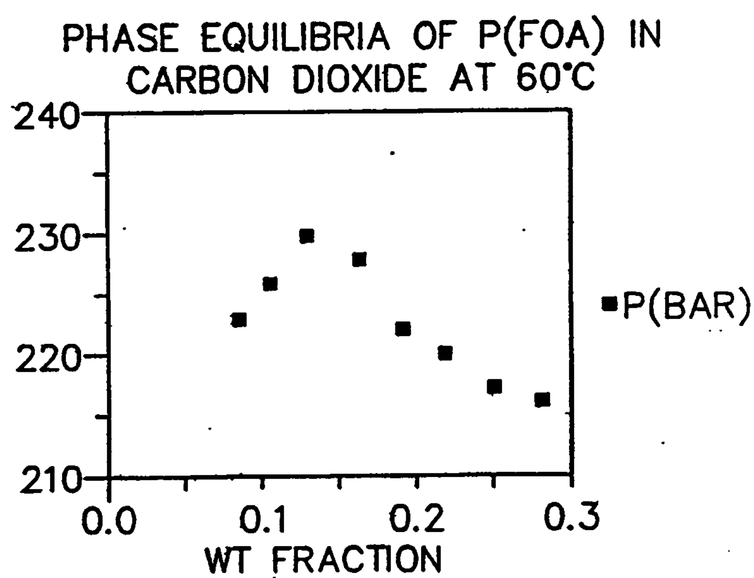

PHASE EQUILIBRIA OF P(FOA) IN CARBON DIOXIDE AT 60°C
240
230
220
210
0.0
0.1
0.2
0.3
WT FRACTION
P(BAR)

FIG. 2.

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08F14/18; C08F20/22; C08F2/06

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	GB,A,1 172 713 (SUMITOMO CHEM. CO. LTD.) 3 December 1969 see claim 1 see page 2, line 58 - page 2, line 76 see page 3, line 13 - page 3, line 21	1-4, 48-50
A	EP,A,0 239 035 (BASF) 30 September 1987	
A	EP,A,0 301 532 (B.F.GOODRICH CO.) 1 February 1989	

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
17 JUNE 1993	3. 07. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	CAUWENBERG C.L.

1

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9301626
SA 71621

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 17/06/93
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-1172713	03-12-69	DE-A,C 1745386	09-03-72
		US-A- 3522228	28-07-70
EP-A-0239035	30-09-87	DE-A- 3609829	24-09-87
		JP-A- 62232413	12-10-87
		US-A- 4748220	31-05-88
EP-A-0301532	01-02-89	AU-A- 2021288	09-02-89
		JP-A- 1163203	27-06-89

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82